Supplementary information

Fabrication of Copper Silicate Microspheres Using Rice Husk Ash and Its Application for Dearomatization of Phenol Derivatives

Na Li,[a] Lide Su,[a] Hongying Wang,[a] Hongdao Li,[b] Qianqian Shen, *[c] and Xiaofeng Han*[a]

Contents

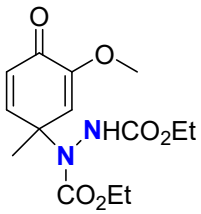
General information

All products were purified by flash chromatography on silica gel (200 - 300 mesh). Reactions were monitored by TLC analysis using silica gel GF-254 thin layer plates. The substrates **3a-3f** were described in the experimental procedures. NMR spectra were recorded with a Quantum-1 plus 400 MHz spectrometers (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR) or a Bruker Ascend^{TM} 500 MHz Spectrometer (500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR). NMR spectra were recorded in deuterated chloroform (7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR) as a solvent and Me_4Si was used as the inert standard, Chemical shifts (δ values) were reported in ppm. Coupling constants in hertz (Hz) were taken from the spectra directly and are uncorrected. Gas Chromatography (GC) was recorded on a GC 2030 from SHIMADZU.

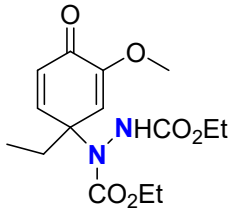
Procedure for the gram-scale reaction of 3a.

To a mixture of phenol (**1a**, 1.38 g, 10 mmol) and diethyl azodicarboxylate (**2**, 3.48 g, 20 mmol) in acetone (8.0 mL) in a 50 mL round-bottom flask, CuSi-NTMs (0.28 g, 20 mol%) was added. The mixture was stirred at room temperature for 2 hours. After the reaction was finished, the organic solvent was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography (ethyl acetate: petroleum ether = 1 : 3) to afford the pure product 3.0 g (92%).

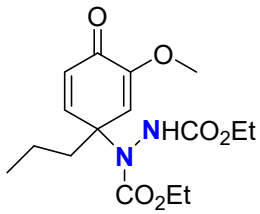
Characterization Data of Products



After purification by column chromatography, the final compound **3a** was obtained as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.02 (m, 2H), 6.87 – 6.61 (m, 1H), 6.13 (m, 1H), 4.18 (m, 2H), 4.06 (m, 2H), 1.84 (m, 3H), 1.47 (m, 3H), 1.27 (m, 3H), 1.11 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.04, 157.25, 155.37, 155.31, 152.02, 151.57, 147.42, 146.90, 133.61, 126.96, 126.86, 62.56, 62.30, 62.09, 60.75, 60.71, 60.40, 25.29, 25.26, 15.60, 14.41, 14.36, 14.12.

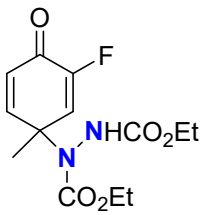


After purification by column chromatography, the final compound **3b** was obtained as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 – 6.77 (m, 2H), 6.68 (d, *J* = 6.4 Hz, 1H), 6.24 (dd, *J* = 10.1, 4.4 Hz, 1H), 4.19 (dtd, *J* = 17.8, 7.1, 4.0 Hz, 4H), 3.64 (d, *J* = 9.3 Hz, 3H), 2.01 (d, *J* = 3.9 Hz, 2H), 1.30 – 1.23 (m, 3H), 1.23 – 1.14 (m, 3H), 0.80 (dt, *J* = 7.4, 3.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.11, 157.33, 155.43, 151.36, 150.52, 128.00, 116.77, 66.04, 62.71, 62.46, 56.25, 55.06, 55.02, 31.49, 30.59, 30.26, 29.74, 28.40, 14.54, 14.25, 8.34, 8.31.

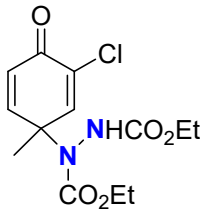


After purification by column chromatography, the final compound **3c** was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 1H), 6.72 – 6.63 (m, 1H), 6.27 – 6.10 (m, 1H), 5.85 – 5.79 (m, 1H), 4.32 – 4.03 (m, 4H), 3.87 – 3.65 (m, 3H), 2.04 – 1.94 (m, 1H), 1.60 (m, 1H), 1.30 – 1.18

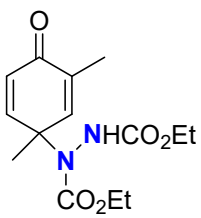
(m, 8H), 0.94 – 0.87 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.17, 157.36, 155.40, 150.98, 127.52, 127.42, 120.19, 117.33, 65.52, 62.60, 62.33, 56.15, 54.95, 54.91, 39.58, 37.51, 24.52, 17.23, 14.47, 14.41, 14.37, 14.35, 14.09.



After purification by column chromatography, the final compound **3d** was obtained as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J = 20.3 Hz, 1H), 6.86 (dd, J = 25.3, 11.4 Hz, 1H), 6.44 (d, J = 12.5 Hz, 1H), 6.16 (dd, J = 17.1, 12.0 Hz, 1H), 4.22 – 4.07 (m, 4H), 1.55 (s, 3H), 1.30 – 1.18 (m, 3H), 1.14 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.45, 178.27, 157.28, 155.07, 154.11, 152.89, 151.98, 126.07, 62.98, 62.56, 62.05, 25.49, 14.45.



After purification by column chromatography, the final compound **3e** was obtained as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 6.56 (m, 3H), 6.24 (dd, *J* = 11.6, 9.9 Hz, 1H), 4.30 – 4.04 (m, 4H), 1.54 (s, 3H), 1.33 – 1.21 (m, 3H), 1.14 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.43, 157.34, 155.36, 152.36, 147.48, 126.12, 63.08, 62.57, 62.30, 25.07, 14.49, 14.47.



After purification by column chromatography, the final compound **3f** was obtained as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 - 6.99 (m, 2H), 6.87 - 6.61 (m, 1H), 6.13 (m, 1H), 4.19 (m, 2H), 4.06 (m, 2H), 1.84 (d, *J* = 6.9 Hz, 3H), 1.47 (m, 3H), 1.27 - 1.23 (m, 3H), 1.11 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.04, 157.25, 155.37, 155.31, 152.02, 151.57, 147.42, 146.90, 133.61, 126.96, 126.86, 62.56, 62.30, 62.09, 60.75, 60.71, 60.40, 25.29, 25.26, 15.60, 14.41, 14.36, 14.12.

Supporting figures

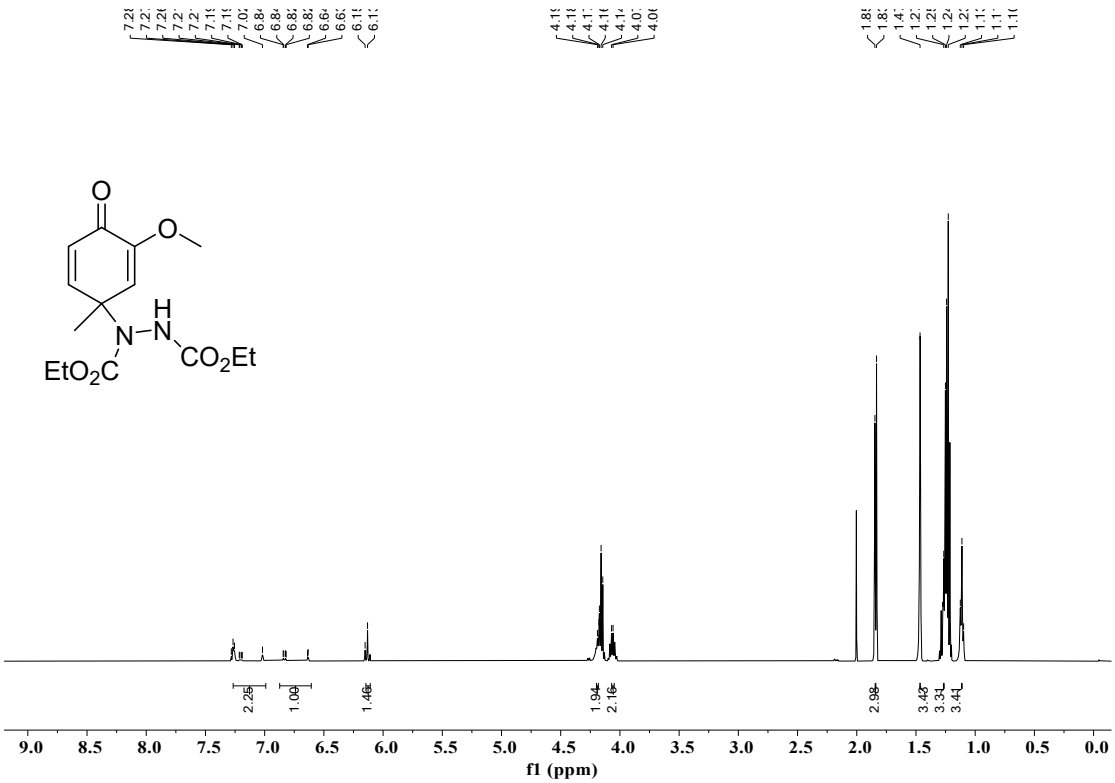


Fig. S1. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

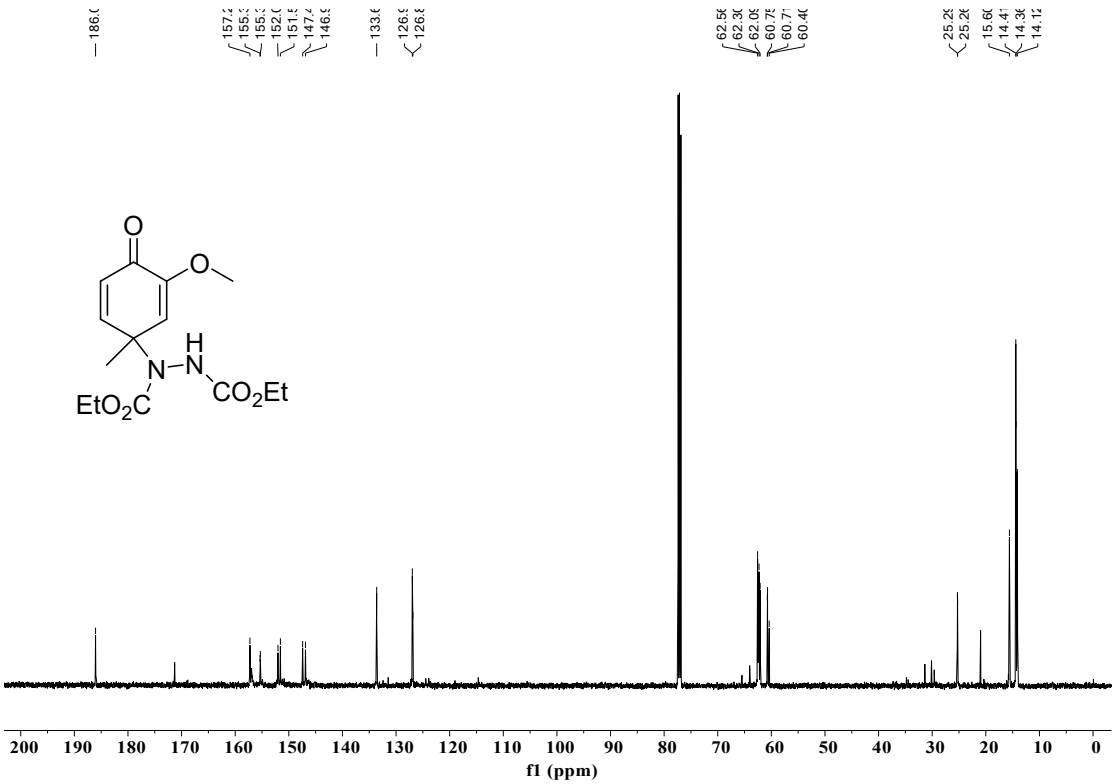


Fig. S2. ^{13}C NMR spectrum of **3a** in $CDCl_3$.

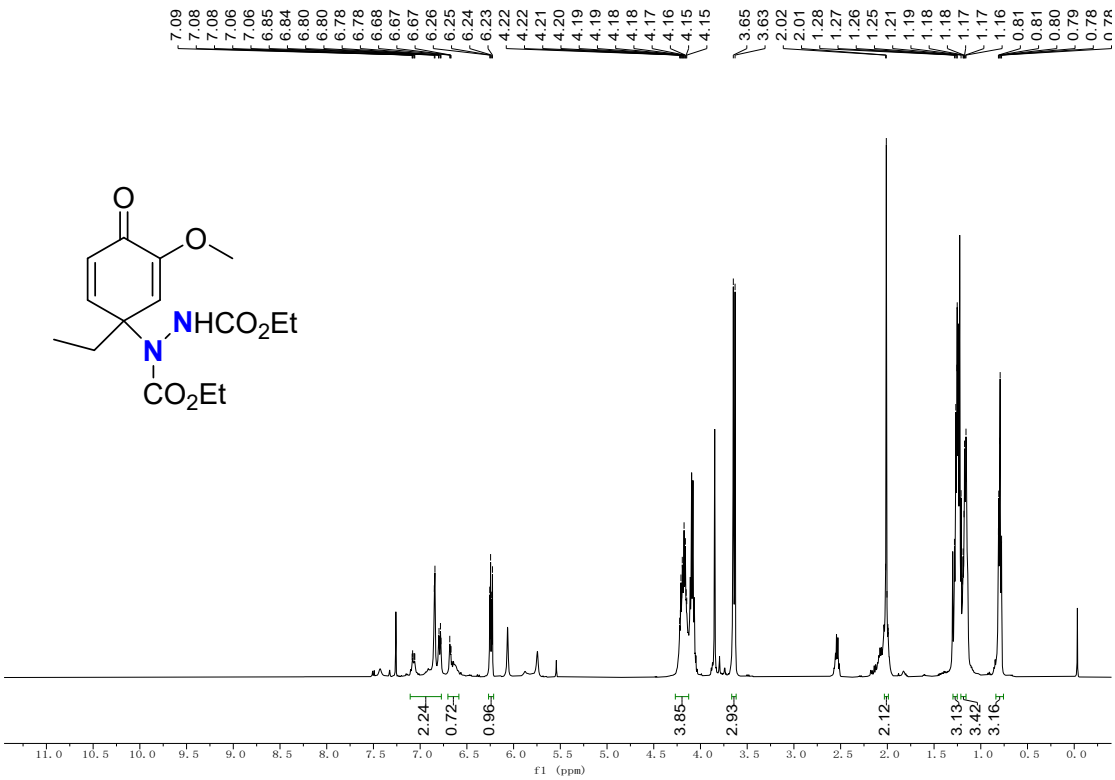


Fig. S3. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

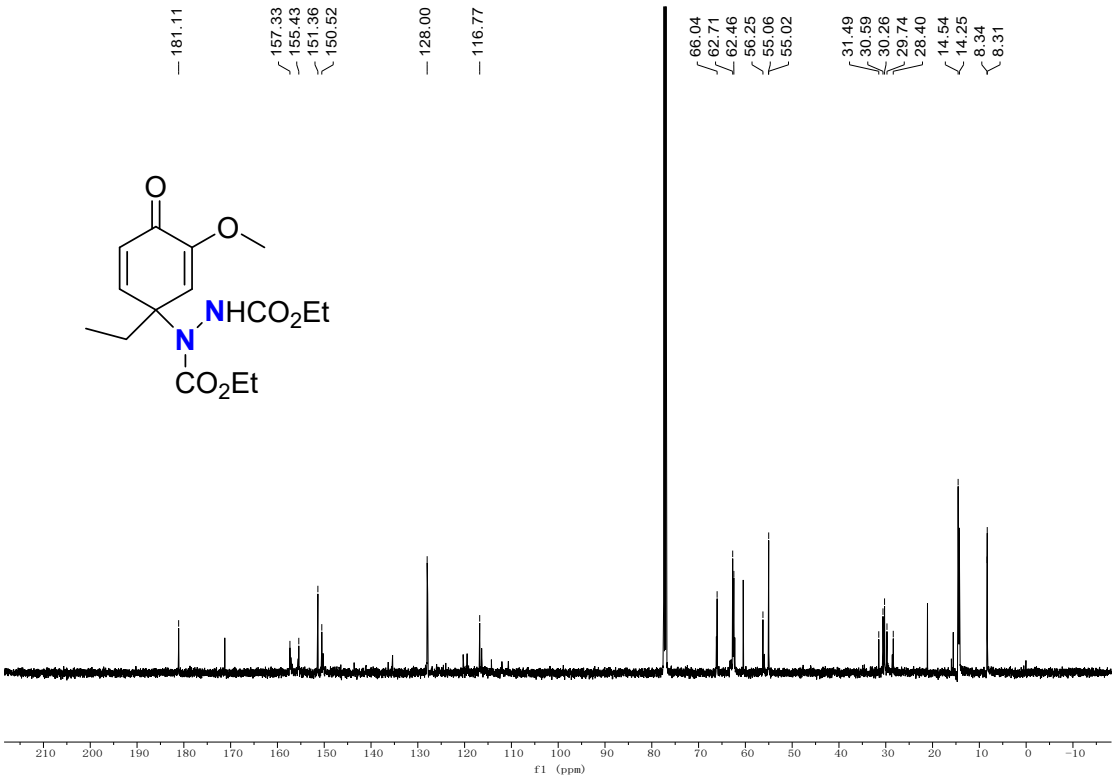


Fig. S4. ^{13}C NMR spectrum of **3b** in $CDCl_3$.

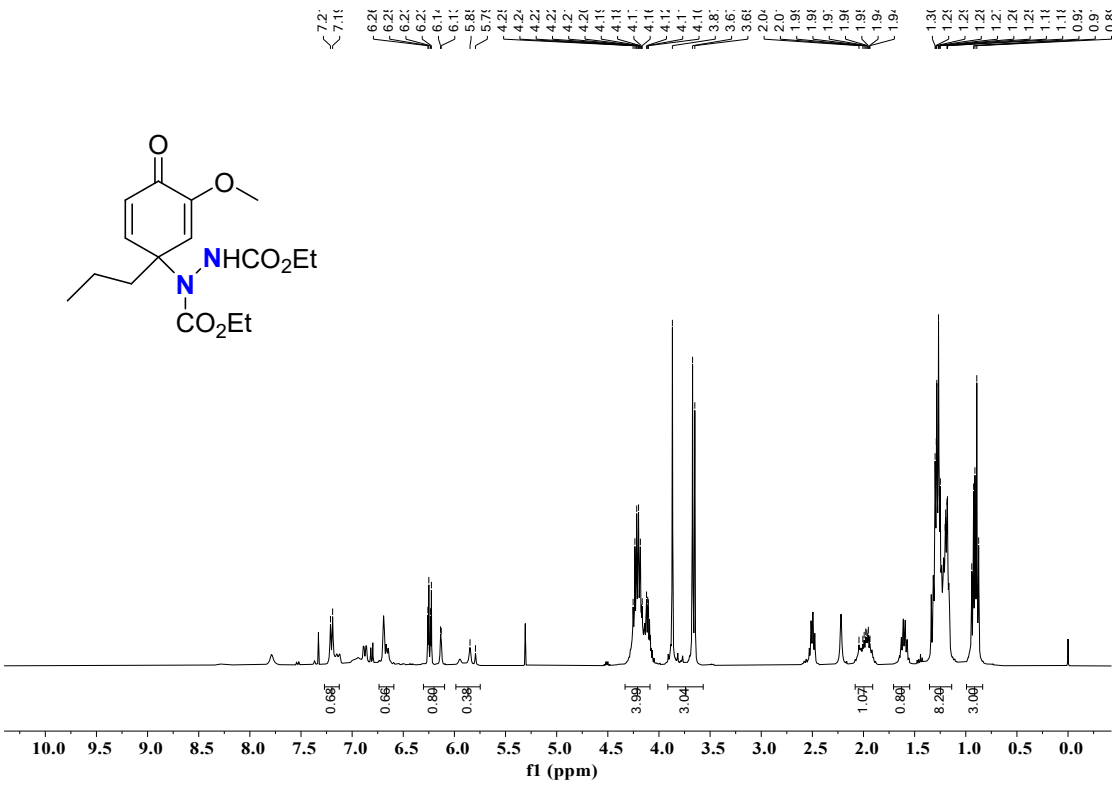


Fig. S5. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

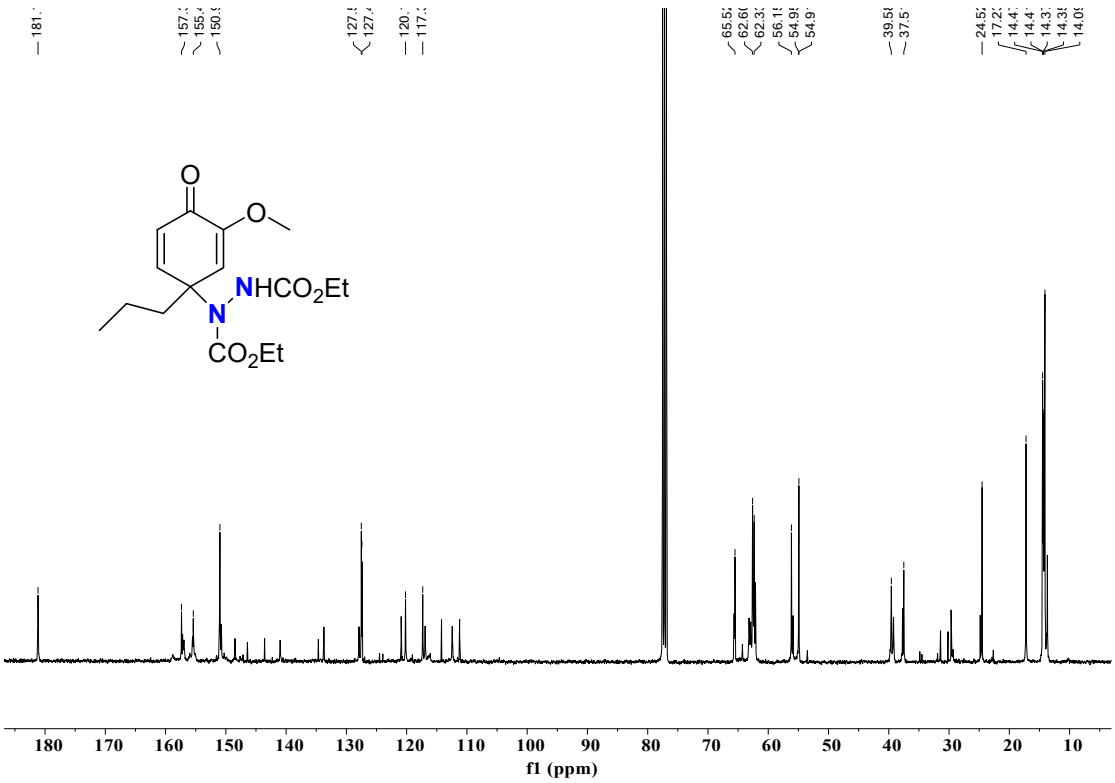


Fig. S6. ^{13}C NMR spectrum of **3c** in $CDCl_3$.

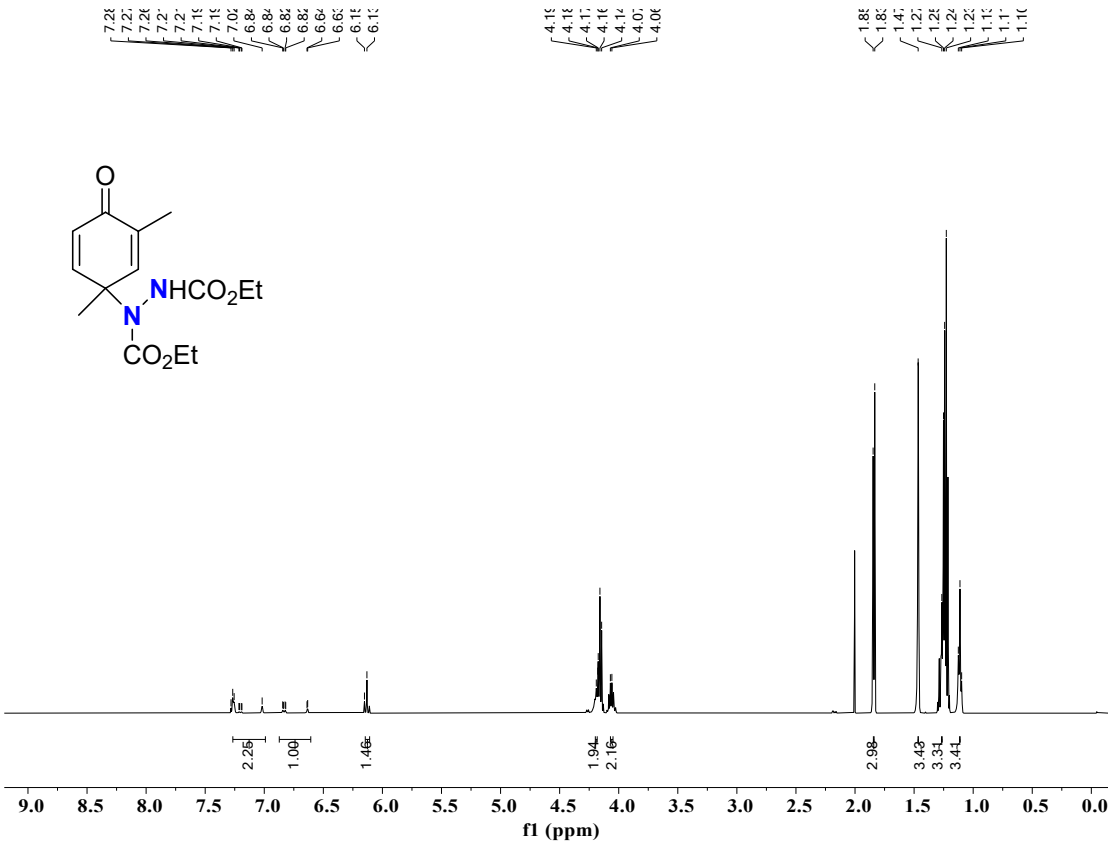


Fig. S7. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

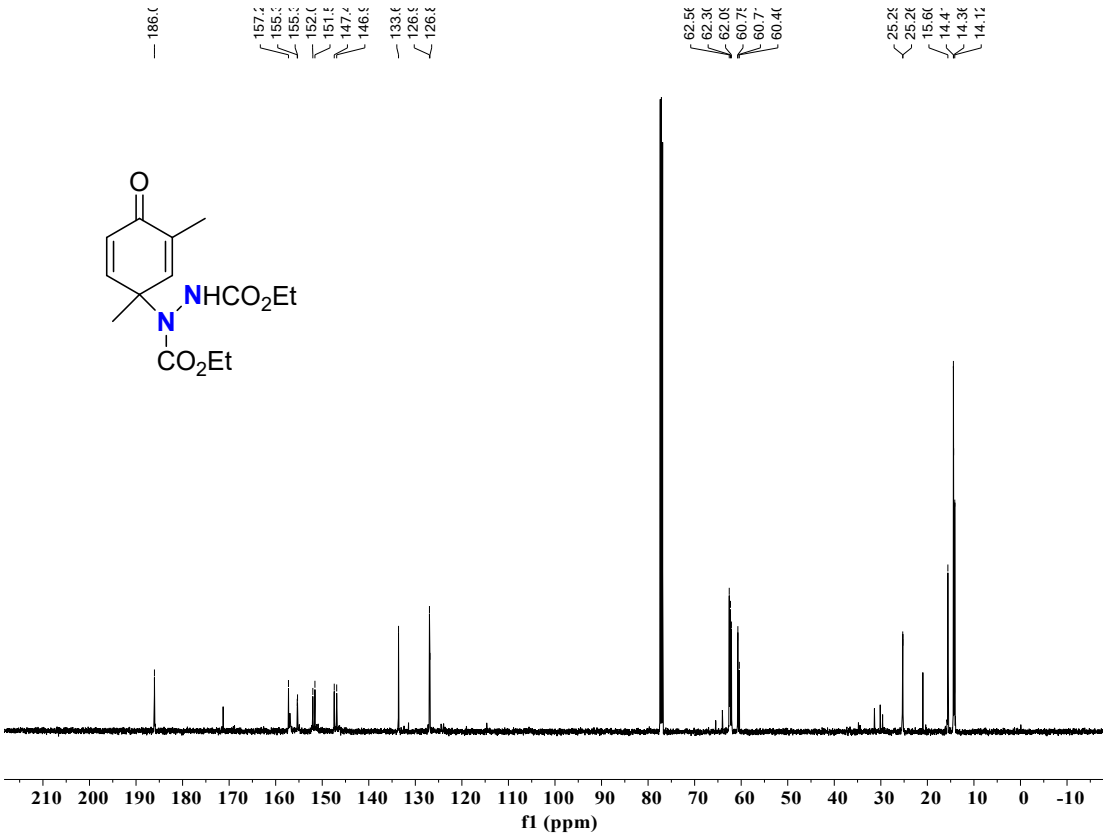


Fig. S8. ^{13}C NMR spectrum of **3d** in $CDCl_3$.

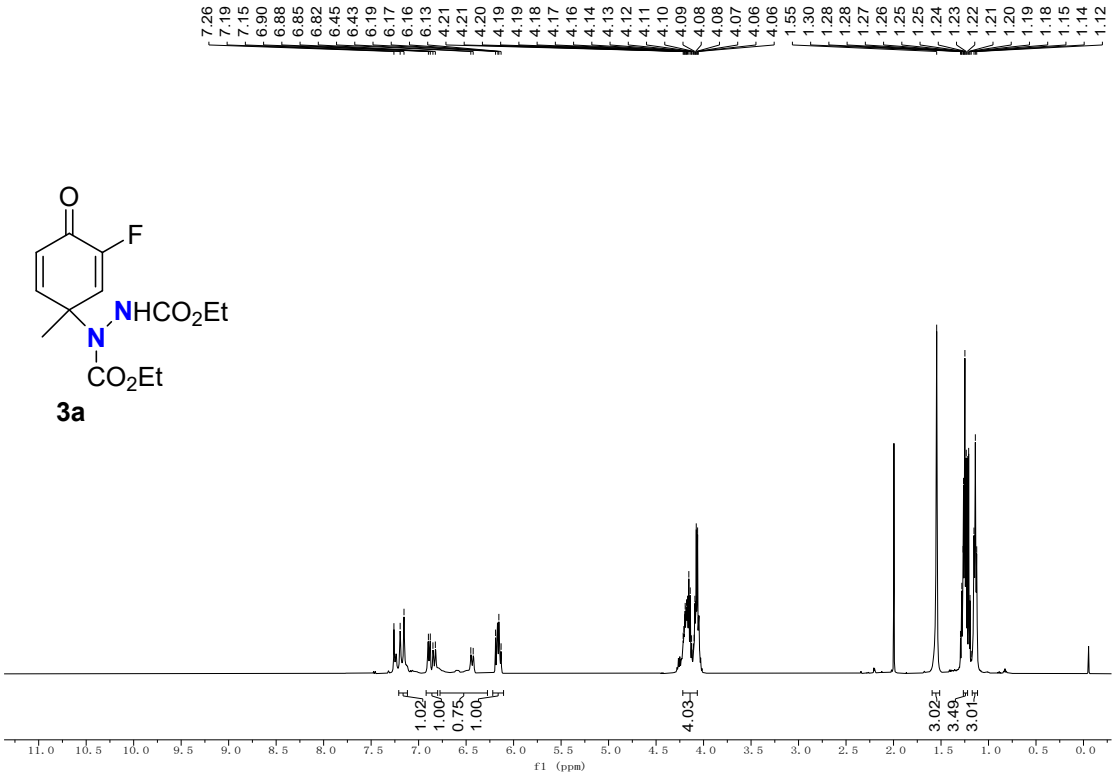


Fig. S9. ^{1}H NMR spectrum of **3e** in $CDCl_3$.

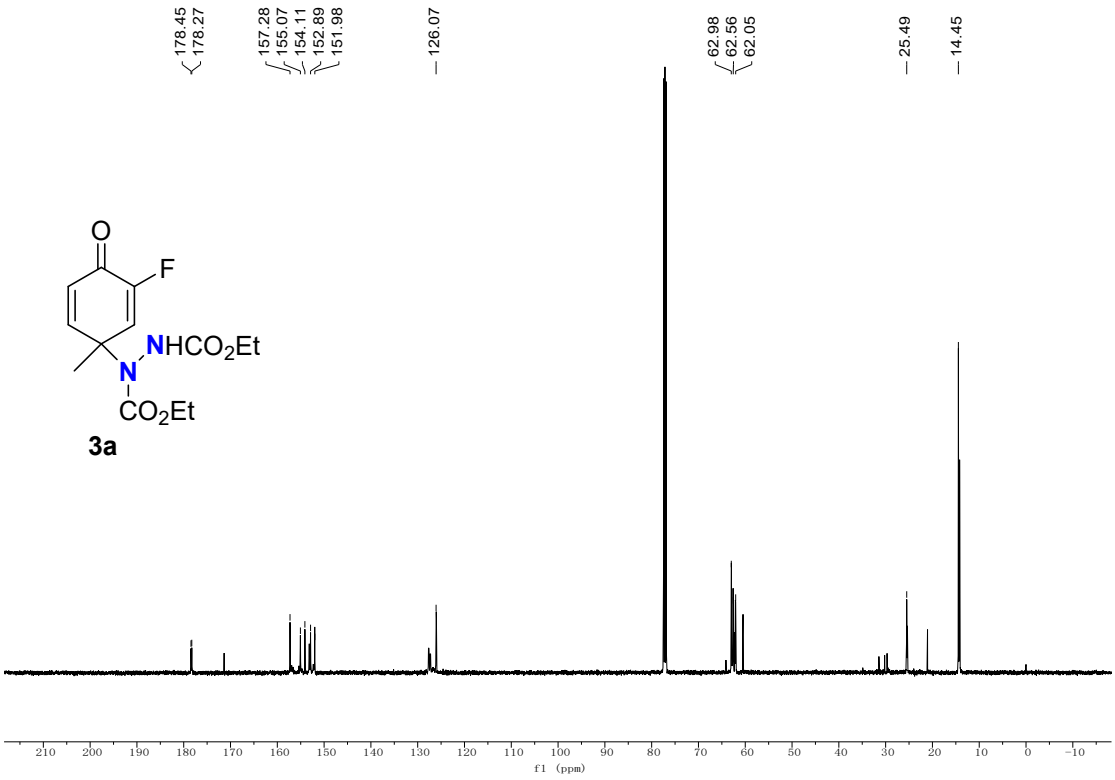


Fig. S10. ^{13}C NMR spectrum of **3e** in $CDCl_3$.

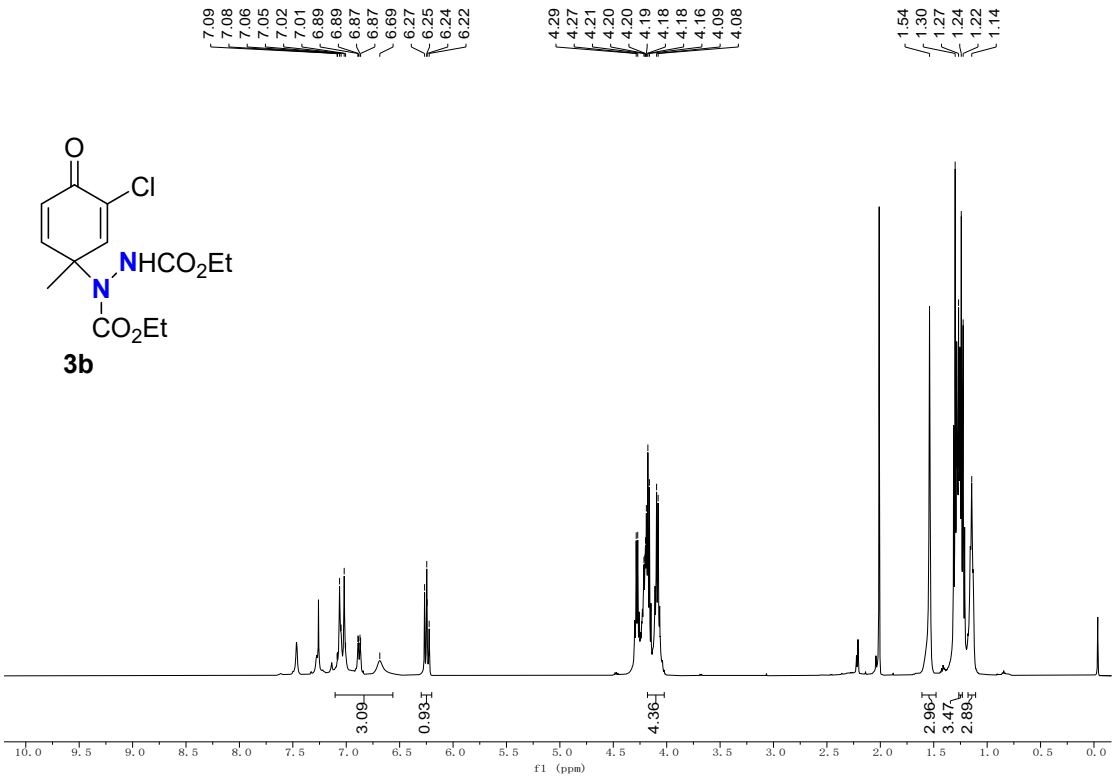


Fig. S11. ^{1}H NMR spectrum of **3f** in $CDCl_3$.

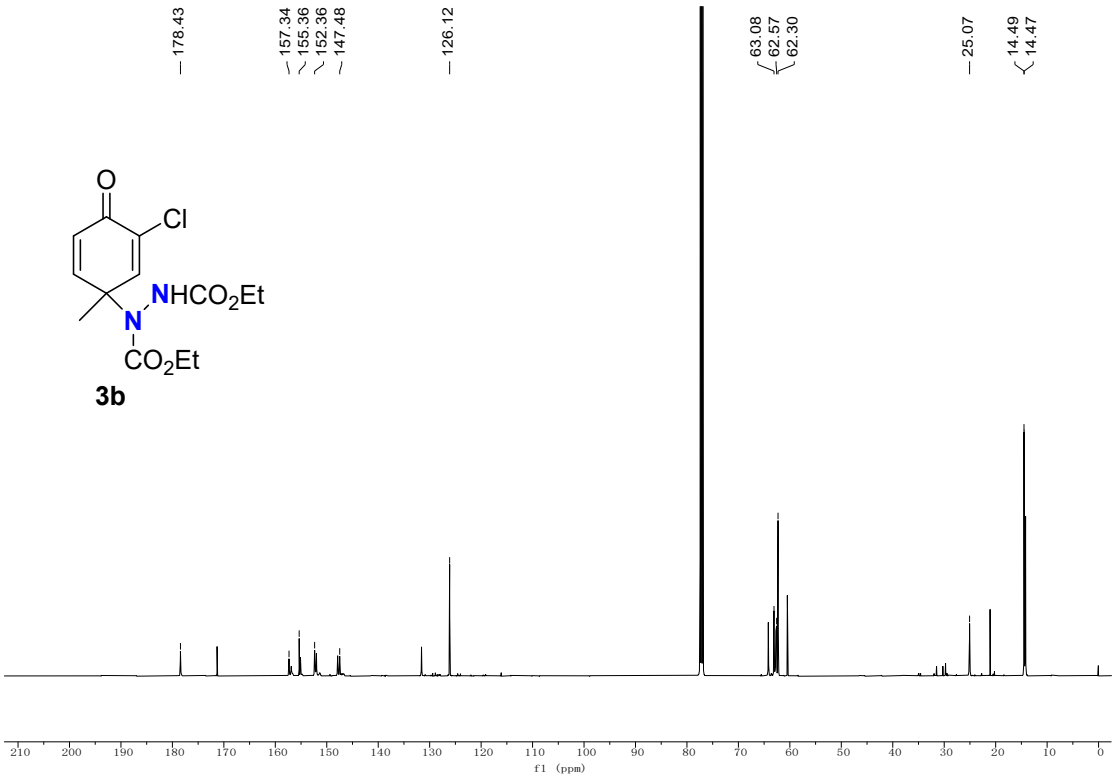


Fig. S12. ^{13}C NMR spectrum of **3f** in $CDCl_3$.

Mechanistic Studies

To a mixture of phenol (**1a**, 0.1 mmol) and diethyl azodicarboxylate (**2**, 0.2 mmol) in acetone (1.0 mL) in a round-bottom flask, CuSi-NTMs (20 mol%) and TEMPO (0.2 mmol) was added. The mixture was stirred at room temperature for 2 hours. After the reaction was finished, 20 µL of the reaction mixture was diluted with 300 µL of EtOAc containing dodecane as an internal standard. The sample was dried over anhydrous Na_2SO_4 and further analyzed by gas chromatography (GC). GC method: The temperature profile was 100 °C holding for 0.5 min; 20 °C min^{-1} to 150°C holding for 2 min; 30 °C min^{-1} to 220°C for 2.0 min.

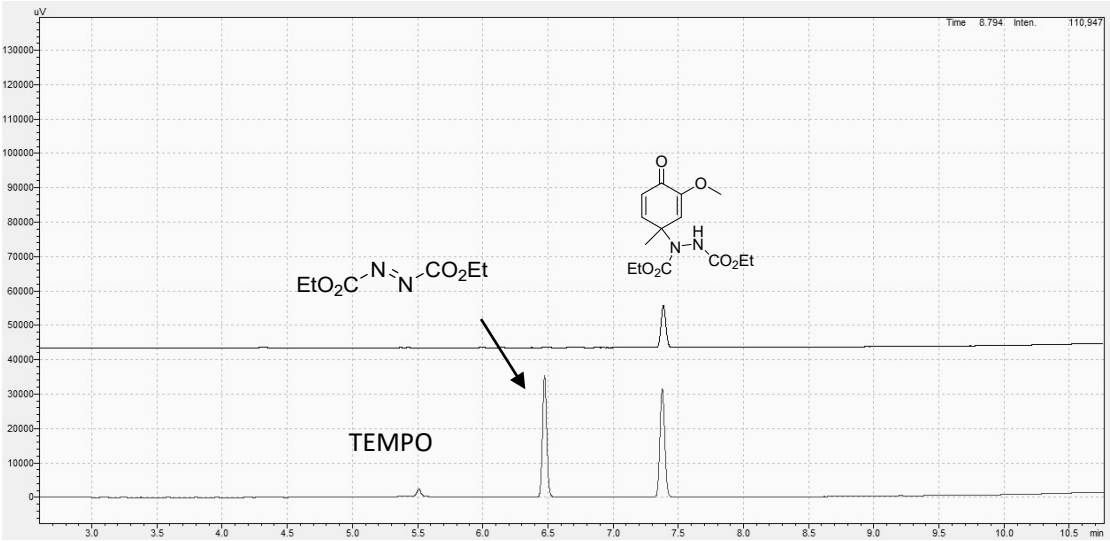


Fig. S13. GC chromatogram of mechanistic studies.